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Entropy (II) - The statistical perspective

Clausius' introducing entropy is purely thermodynamic. It microscopic origin remains elusive. In comparison, internal energy has a much clearer microscopic picture. Boltzmann pointed out that entropy is the logarithm of the number of microscopic states, which bridges the thermodynamic definition and the microscopic picture of entropy.

5.1 Statistical meaning of entropy

Boltzmann provided a probability interpretation of entropy, which later became widely applied in physics and information sciences. Suppose a system has equal probability among W states, then its entropy is defined as

$$S/k_B = \ln W, \tag{5.1}$$

where k_B is Boltzmann constant carrying the unit of entropy. This formula is inscribed on Boltzmann's tombstone.

It is mysterious how Boltzmann discovered this remarkable relation of Eq. 5.1. Let me imagine a possible motivation. Consider an isothermal expansion of an ideal gas at temperature T from the volume V_0 to V_1, the entropy change reads

$$\frac{\Delta S}{k_B} = \frac{Q}{k_B T} = -\frac{W}{k_B T} = N \ln \frac{V_1}{V_0}. \tag{5.2}$$

In the volume doubles, the possible configuration space of a molecule also doubles, then the entropy increase per molecule is $k_B \ln 2$. Based on this observation, it is reasonable to speculate Eq. (5.1).

Next we generalize the Boltzman formula of Eq. (5.1) to the case that different states are taken at different probabilities. Consider a system has the

Figure 5.1 Tombstone of Ludwig Boltzmann (1844-1906) on which $S = k \ln W$ is inscribed. Unfortunately, he committed suicide, after a long term defending his theory. He felt tired and depressed....

probability p_i lying in state i for $i = 1, 2, ...n$, where $\sum_{i=1}^{n} p_i = 1$. How to calculate the entropy?

Let us replica the system to N copies with N a very large number. This N-copies put together is called an ensemble. In this ensemble, there are Np_i systems lying in state i if N is very very large. Hence, the configuration number of the ensemble is

$$W = \frac{N!}{\Pi_{i=1}^{n}(Np_i)!}. \tag{5.3}$$

Then applying the Boltzman entropy formula, we arrive at the entropy of the ensemble as

$$\frac{S_E}{k_B} = \ln \frac{N!}{\Pi_{i=1}^{n}(Np_i)!} = \ln N! - \sum_{i=1}^{n} \ln(Np_i)!. \tag{5.4}$$

We need to further expand Eq. 5.4. Correct to the order of $O(\ln N)$, the following equation holds

$$\ln N! \approx N \ln N - N + \frac{1}{2} \ln N + O(\ln N), \tag{5.5}$$

Here is a simply way to derive Eq. 5.5,

$$\ln N! = \sum_{j=1}^{N} \ln j. \tag{5.6}$$

Use the trapezoid method to approximate the integral

$$\begin{aligned}\int_M^{M+1} \ln x dx &= (M+1)\ln(M+1) - M\ln M - 1 \\ &\approx \ln M + \frac{1}{2M} + O(1/M^2) \\ &\approx \frac{1}{2}(\ln M + \ln(M+1)) + O(1/M^2)\end{aligned} \tag{5.7}$$

Summing over M from 1 to $N-1$, we arrive at

$$\begin{aligned}\int_1^N \ln x dx &= N\ln N - N + 1 \\ &= \frac{1}{2}\ln 1 + \ln 2 + ... + \ln(N-1) + \frac{1}{2}\ln N + C,\end{aligned} \tag{5.8}$$

where C is the sum of errors of each step. Since the error of each step scales as $1/M^2$, its sum converges as $N \to \infty$, hence C is a constant. Then we arrive at the logarithmic version of the Stirling formula correct to $O(\ln N)$.

Applying Eq. 5.5, we arrive at $S_E/(Nk_B) = -\sum_i p_i \ln p_i$. The entropy for the system S is just S_E/N, we have

$$S = -\sum_{i=1}^{n} p_i \ln p_i. \tag{5.9}$$

If all the states are with the equal probability, i.e., $p = 1/n$, then the entropy formula is reduced back to the Boltzmann form Eq. (5.1).

5.2 Thermodynamics meets statistics

The Boltzmann's interpretation of entropy is impressive. Nevertheless, it has a big gap with its original thermodynamic meaning. How to bridge the microscopic and macroscopic physics?

Now we introduce the concept of ensemble, which is the foundation of modern statistical mechanics. The theory of ensemble was developed by Josiah Gibbs in 1870's. Consider a system, and duplicate it into N identical copies. According to different relations among the copies, Gibbs defined different types of ensembles.

(i) Microcanonical(NVE) ensemble: Every system in the ensemble must be strictly isolated with its environment without heat and particle exchange, i.e., the total energy (E) and the particle number (N) in each system is fixed.

(ii) Canonical (NVT) ensemble: The series of systems 1, 2, 3, ... N in the ensemble are thermally connected. There can be heat transfer among them to reach thermal equilibrium, sharing the same temperature T, i.e., each system may have different energy. They should have no particle exchange, i.e., the particle number N in each system remains fixed.

(iii) Grand canonical (μVT) ensemble: There exist both heat and particle number exchange between different systems in the ensemble. Neither energy and particle number are fixed in each systems. Instead, they reach thermal and chemical equilibriums such that all the systems share the same temperature T and the chemical potential μ.

There may also exist other types of ensembles. For example, in chemical reactions the volume is often not fixed, but the pressure is fixed. You may define Gibbs ensemble, also called, isobaric-isothermal ensemble, in which every system has fixed pressure (P), particle number (N), and temperature (T).

Now let employ the perspective of canonical ensemble such that a system therein is characterized by temperature T, particle number N, and volume V. Even though the energy of each system E_i is not conserved, their total energy remains fixed, i.e., the following constraint exists,

$$\sum_{i=1}^{N} E_i = E_0, \tag{5.10}$$

where E_0 is a constant.

The ensemble as an entire object is isolated from the environment. Since its total energy is conserve, any state of the ensemble (*not the state of a system*) should be treated at equal footing. Hence, the probability ρ of an ensemble state is a constant as long as the constraint of Eq. (5.10) is satisfied,

$$\rho = C\delta(E - E_0)\Pi_{i=1}^{N}\Gamma_i, \tag{5.11}$$

where C is a normalization constant, $\Delta\Gamma_i$ is the number of states of the i-th system at the energy E_i. Then according to the Boltzmann formula,

$$\Gamma_i(E_i) = e^{S_i(E_i)/k_B}, \tag{5.12}$$

in which a small broadening of energy ΔE_i is assumed.

Define the entropy of the ensemble $S(E_1, E_2, ...E_N)$ as

$$S(E_1, E_2, ...E_N) = \sum_{i=1}^{N} S_i(E_i). \tag{5.13}$$

At thermal equilibrium, we want the entropy reach the maximum. Hence, we use the Lagragian multiplier method by introducing β,

$$f(E_1, E_2, ...E_N) = S(E_1, E_2, ...E_N) - k_B\beta(\sum_{i=1}^{N} E_i - E_0). \tag{5.14}$$

The maxima of entropy is reached at

$$\frac{\partial S(E_1, ..E_N)}{\partial E_i} = \frac{\partial S_i(E_i)}{\partial E_i} = k_B\beta. \tag{5.15}$$

Hence, β is a common factor shared by all the systems at thermal equilibrium. According to the 1st law of thermodynamics of the reversible process, $T = (\partial E/\partial S)_V$, we make the correspondence

$$k_B\beta = \frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V, \tag{5.16}$$

(Note we use the symbol E as internal energy here.).

5.3 Boltzmann distribution via canonical ensemble

Consider a canonical ensemble. The duplications of N copies of the system you want to study, which reaches thermal equilibrium via thermal contact. Pick up one system S for study, and treat all the others together as the heat reservoir R. The energy of the system S is denoted as E and that of the reservoir is denoted as E_R, hence,

$$E + E_R = E_0, \tag{5.17}$$

where E_0 is fixed.

The system S may be in a set of states 1, 2, ..., n.... We would like to figure out the probability for system S lying in state n with the energy $E_{S,n}$. Since the system plus the reservoir together is an isolated big system, all the states with the same $E_n + E_R = E_0$ are at equal probability. Hence, the probability of the system S staying at state n is proportional to how many states of the reservoir R at the energy of $E_0 - E_n$. Using the Boltzmann formula, the number of states is represented by putting entropy on the exponent, i.e.,

$$\rho_n = Ce^{S_R(E_0 - E_n)/k_B}, \tag{5.18}$$

where C is a normalization constant. Since E_n is a small quantity relative to E_0, the entropy S_R can be expanded as

$$S_R(E_0 - E_n) = S_R(E_0) - \frac{\partial S_R}{\partial E}|_{E_0} E_n, \tag{5.19}$$

then

$$\rho_n = Z^{-1} e^{-\beta E_n}, \tag{5.20}$$

where Z as a function of temperature is called the partition function,

$$Z(\beta) = \sum_n e^{-\beta E_n}. \tag{5.21}$$

This distribution is called the Boltzmann distribution.

Remember the entropy formula $S/k_B = -\sum_n \rho_n \ln \rho_n$ derived before, and plug in $\rho_n = Z^{-1} e^{-\beta E_n}$, then we arrive at

$$S/k_B = -\sum_n \rho_n (\ln Z^{-1} - \beta E_n) = \ln Z - \beta \langle E \rangle = \ln Z - \beta U. \tag{5.22}$$

Hence, $-k_B T \ln Z = U - TS$. This quantity is denoted as the free energy, i.e.,

$$F = U - TS. \tag{5.23}$$

The free energy F is crucially important for a system at the thermal equilibrium with temperature T. Here we provide an intuitive and crude explanation. We divide the energy E into many small steps of ΔE, and reexpress the partition function in Eq. 5.21 as

$$Z = \sum \Delta E g(E) e^{-\beta E} = \sum e^{-\beta[E - k_B T \ln(\Delta E g(E))]} = \sum e^{-\beta[E - TS(E)]}, \tag{5.24}$$

where ΔE is a small energy step, and $\Delta E g(E)$ is the number of states within the energy interval from E to $E + \Delta E$.

Assume the contribution to the summation is peaked within the interval $\bar{E} \pm \frac{1}{2}\Delta E$, where ΔE is the width of fluctuations. $\bar{E}$ is the mean value and roughly speaking, it is also the most probable value. For a macroscopic system, ΔE scales as $N^{1/2}$ and $\bar{E}$ scales as N, then $\Delta E / \bar{E} \propto N^{-1/2}$, hence, the relative fluctuation goes to zero. Then the most probable energy $\bar{E}$ place occurs when $E - k_B T \ln[\Delta E g(E)]$ takes the minimal value. Since $k_B \ln[\Delta E g(E)]$ is just the Boltzmann's definition of entropy, hence, the free energy reaches minimum at thermal equilibrium. Hence at a finite temperature, there exists a competition between energy E and the entropy S. The interplay between them gives rise to a variety of rich physics of transitions of states of matter.

Based on the differential form of the 1st law of thermodynaics for reversible process,

$$dU = -pdV + TdS, \tag{5.25}$$

the differential form of the free energy F is obtained,

$$dF = dU - d(TS) = -pdV - SdT. \tag{5.26}$$

Hence, entropy can be calculated via

$$S = -\left(\frac{\partial F}{\partial T}\right)_V \tag{5.27}$$

5.4 Free energy of an ideal gas

For a classic system such as an ideal monoatomic gas with N atoms, its states are represented in the phase space of N-particles represented by $(\mathbf{r}_1, \mathbf{p}_1; ..., \mathbf{r}_N, \mathbf{p}_N)$. For an ideal gas, the probability distribution function can be factorized into that of each particle,

$$\rho(\mathbf{r}_1, \mathbf{p}_1; ..., \mathbf{r}_N, \mathbf{p}_N) = \Pi_{i=1}^N \rho(\mathbf{r}_i, \mathbf{p}_i) = \Pi_{i=1}^N \rho(\mathbf{r}_i)\rho(\mathbf{p}_i). \tag{5.28}$$

In free space, $\rho(\mathbf{r}_i) = 1/V$ is a constant, where V is the system volume. The single particle probability distribution function is

$$\rho(\mathbf{r}_i, \mathbf{p}_i) = \frac{1}{Z_1} \exp\left(-\beta\left(\frac{p_x^2 + p_y^2 + p_z^2}{2m}\right)\right), \tag{5.29}$$

where

$$Z_1 = V \iiint dp_x dp_y dp_z \exp\left(-\beta\left(\frac{p_x^2 + p_y^2 + p_z^2}{2m}\right)\right) = V\,(2\pi m k_B T)^{3/2} \tag{5.30}$$

Nevertheless, for an N-particle system, the partition function is defined as

$$Z_N = \frac{1}{N!}\Pi_i \int \frac{d\mathbf{p}_i d\mathbf{q}_i}{(2\pi\hbar)^3} e^{-\frac{\beta}{2m}\sum_{i=1}^N \mathbf{p}_i^2}. \tag{5.31}$$

Here the factor of $1/N!$ is a quantum mechanical feature that all particles of the same kind are indistinguishable. The factor of $(2\pi\hbar)^3$ represent the volume of a quantum state in a single particle phase space.

It can be integrated that

$$Z_N = \frac{1}{N!}\left(\frac{V}{\lambda_T^3}\right)^N, \tag{5.32}$$

where λ_T is called the thermal wavelength defined as

$$\lambda_T = \frac{h}{\sqrt{2m\pi k_B T}}. \tag{5.33}$$

The free energy F is

$$\begin{aligned}\frac{F}{N} &= -\frac{k_B T}{N}\ln Z_N = k_B T\left(\frac{\ln N!}{N} - \ln\frac{V}{\lambda_T^3}\right) = k_B T\left(\ln N - 1 - \ln\frac{V}{\lambda_T^3}\right)\\ &= k_B T\left[\ln\left(\lambda_T^3 n\right) - 1\right].\end{aligned} \tag{5.34}$$